

THERMOPLASTIC ELASTOMER RESIN**TECHNICAL FIELD**

5 The present invention relates to a novel thermoplastic elastomer resin and a process for preparing thereof, which resin is suitable for automobile parts, particularly constant velocity joint boots and bellows, because it has good melt viscosity, melt tension, and thermal resistance. More particularly, the present invention relates to a thermoplastic elastomer resin having good properties and to a process for preparing thereof, which
10 comprises subjecting bisphenol-alt-ethylene glycol oligomer to melt polymerization, and subjecting the polymerized product to reactive extrusion by using hydroxy carboxylic acid compound, diisocyanate, and carbodiimide.

BACKGROUND ART

15 Polyester-type thermoplastic elastomer (below "TPE") has good oil resistance and chemical resistance as well as excellent low temperature impact property. Thus, it has been widely used in automobile and electric/electronic fields. However, particularly chloroprene rubber (CR), which has been widely used for automobile parts, has poor
20 durability. Thus, recently CR has been replaced with TPE. The use of TPE has been expanded in North America and Europe since it has a good light weight property, resistant-fatigability, chemical resistance, and ozone resistance, compared with CR. Particularly, since TPE for extrusion blowing is produced through blowing procedure in the melting state, resin should have good melt viscosity and melt tension in the melting
25 state, and the thickness distribution of processed product during extrusion blowing should be constant.

 Generally speaking, TPE cannot be subjected to extrusion-blowing due to its low melt viscosity and melt tension in the melting state. The melt viscosity or melt tension of

extender and stabilizer for hydrolysis with hydroxy carboxylic acid compound to the polymerized product in order to use it for blowing through increasing the molecular weight, after forming thermoplastic elastomer resin (TPE-A) comprising aromatic dicarboxylic acid, diol having a low molecular weight, polyalkylene oxide, and bisphenol-alt-ethylene glycol oligomer through melt polymerization, in preparing thermoplastic elastomer. The present invention was completed on the basis of the above discovery.

In the present invention, hydroxy carboxylic acid compound that is added at the reactive extrusion maintains the number of hydroxyl group that may react with isocyanate group optimal, thereby to make reactivity of diisocyanate, chain extender, optimal. Also, because carbodiimide is used in order to increase hydrolytic resistance, the chain extender and stabilizer for hydrolysis may fully react with elastomers in the twin screw extruder to produce thermoplastic elastomer having good thermal resistance and no variation in physical property of the product. Also, hardness may be easily and freely controlled by introducing hydroxy carboxylic acid compound at the time of preparing thermoplastic elastomer resin (TPE-B). The hardness of thermoplastic elastomer resin (TPE-B) may be controlled by the content of polyalkyleneoxide that is introduced at the time of preparing thermoplastic elastomer resin (TPE-A). Thus, to produce elastomers with different levels of hardness depending on use, previously polymerization reaction had been carried out by adjusting the content of polyalkyleneoxide. However, the present invention has an advantage that hardness may be controlled through a reaction for a short period of time, instead of controlling the content of polyalkyleneoxide, by using hydroxy carboxylic acid compound at the reactive extrusion.

Therefore, one object of the present invention is to provide thermoplastic elastomer resin (TPE-A) characterized in comprising aromatic dicarboxylic acid, diol having a low molecular weight, and 0.3 ~ 9.0 weight% of bisphenol-alt-ethylene glycol oligomer with polyalkyleneoxide.

It is another object of the present invention to provide thermoplastic elastomer resin (TPE-B) suitable for automobile parts, particularly constant velocity joint boots and

bellows since it has good melt viscosity, melt tension and thermal resistance characterized in that it comprises hydroxy carboxylic acid compound, diisocyanate and carbodiimide with the above TPE-A.

5 It is still another object of the present invention to provide a process for preparing the above thermoplastic elastomer resin (TPE-B).

BEST MODE FOR CARRYING OUT THE INVENTION

10 Thermoplastic elastomer resin (TPE-A) according to the present invention comprises aromatic dicarboxylic acid, diol having a low molecular weight, polyalkylene oxide, and bisphenol-alt-ethylene glycol oligomer. Thermoplastic elastomer resin (TPE-B) comprises hydroxy carboxylic acid compound, diisocyanate, and carbodiimide, with the above thermoplastic elastomer resin (TPE-A).

15 Thermoplastic elastomer resin is thermoplastic polymer which hard segment and soft segment is block copolymerized. Thermoplastic elastomer resin (TPE) according to the present invention uses aromatic dicarboxylic acid and diol having a low molecular weight as a hard segment component, and polyalkylene oxide as a soft segment
20 component.

The aromatic dicarboxylic acid may include terephthalic acid (TPA), isophthalic acid (IPA), 1,5-dinaphthalenedicarboxylic acid (1,5-NDCA), 2,6-naphthalenedicarboxylic acid (2,6-NDCA), and dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI), in
25 which diacid is replaced with dimethyl group, and mixture thereof, but DMT is preferable. In preparing thermoplastic elastomer resin (TPE-A) according to the present invention, aromatic dicarboxylic acid is used in the amount of 30 ~ 45 weight%, preferably 33 ~ 40 weight%. If the aromatic dicarboxylic acid is used in the amount less than 30 weight% or over 45 weight%, the reaction balance is lost to disturb the reaction.

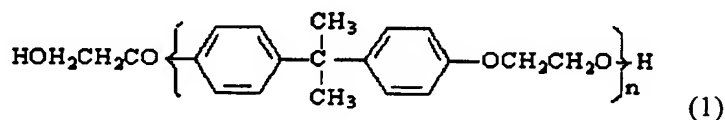
30 Diol having a low molecular weight according to the present invention includes

ethyleneglycol, propyleneglycol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, and 1,4-cyclohexanedimethanol, but 1,4-butane diol is preferable. Diol having a low molecular weight is used in the amount of 15 ~ 30 weight%, preferably 20 ~ 25 weight%. If diol having a low molecular weight less than 15 weight% or over 30 weight% is used, the reaction balance is lost to disturb the reaction, as in aromatic dicarboxylic acid.

As polyalkylene oxide may be used polyoxyethylene glycol, polyoxypropylene glycol, polyoxytetramethylene glycol (PTMEG), etc. PTMEG is preferably used among those. Particularly, it is preferable for PTMEG to have a number average molecular weight of 1,000~3,000, and more preferable of 2,000. Generally speaking, the hardness of polyester-type elastomer is expressed by Shore hardness-D (Shore-D), which is determined by the content of polyalkylene oxide. That is, the more the content of polyalkylene oxide is, the lower the hardness (Shore hardness-D) is.

In preparing thermoplastic elastomer resin (TPE-A) according to the present invention, 20 ~ 50 weight%, preferably 30 ~ 45 weight%, of polyalkylene oxide is used. If polyalkylene oxide is present in the amount less than 20 weight%, the hardness of TPE is high, and thus the resistance against wear due to friction in the product after polymer processing gets high. If over 50 weight%, it could be a problem that the thermal resistance of TPE itself is low.

Bisphenol-alt-ethylene glycol oligomer can be represented by the following formula (1):



wherein, n denotes a positive integer of 1 to 5, preferably 1 to 3.

In preparing TPE-A according to the present invention, bisphenol-alt-ethylene glycol oligomer of the above formula (1) reacts with aromatic dicarboxylic acid. A part of aromatic dicarboxylic acid and of hard segment of diol having a low molecular weight is substituted by bisphenol-alt-ethylene glycol oligomer, which makes thermal-resistance good.

When preparing TPE-A according to the present invention, the bisphenol-alt-ethylene glycol oligomer is used in the amount of 0.3 ~ 9.0 weight%, preferably 0.5 ~ 5.0 weight%, more preferably 1.5 ~ 4.0 weight%. In case that bisphenol-alt-ethylene glycol oligomer is less than 0.3 weight%, the improvement of elastic recovery rate and processability is insignificant. In case that over 9.0 weight%, it is difficult to control the hardness of TPE.

For the thermoplastic elastomer resin (TPE-A) according to the present invention, additives such as branching agent may also be used. Branching agent may increase the melt viscosity and melt tension of elastomer. As branching agent, glycerol, pentaerythritol, neopentylglycol, etc., preferably glycerol, may be used in the amount of 0.05 ~ 0.10 weight%. If the branching agent is less than 0.05 weight%, it is hard to expect the increase of melt viscosity. If over 0.10 weight%, the melt viscosity of TPE-A is so overly raised that it is difficult to control the inherent viscosity at melting polymerization.

The preparation process of thermoplastic elastomer resin (TPE-A) according to the present invention consists of two steps, oligomerization and polycondensation. Oligomerization is carried out at 140 ~ 215 °C for 3~4 hours by using 0.025 ~ 0.03 weight% of titanium butoxide (TBT) as catalyst. Polycondensation is processed by reducing the pressure stepwise from 760 torr to 0.3 torr.

and may cause appearance defect of the processed product due to generation of smell and gas at polymer processing, may be generated by the decomposition of PTMEG. Thus, the present invention uses such a polycondensation process that in order to suppress the generation of THF up to the maximum, the pressure is reduced from 760 torr to 0.3 torr for 1 hour, the vacuum condition of 0.3 torr or less is applied for additional 3 ~ 4 hours, the temperature of reactor is raised from 210 °C to 250 °C for 2 hours, and the final temperature of 250 °C is maintained for the remaining 2 ~ 3 hours.

Branched polyester-type elastomer (TPE-A) is prepared according to the above melt polymerization, with containing 30 ~ 45 weight% of aromatic dicarboxylic acid, 15 ~ 30 weight% of diol having a low molecular weight, 20 ~ 50 weight% of polyalkylene oxide, and 0.3 ~ 9.0 weight% of bisphenol-alt-ethylene glycol oligomer, represented by the formula (1). TPE-A is obtained by predicting its molecular weight on the basis of Torque applied to the stirrer of polycondensation reactor. The molecular weight of obtained thermoplastic elastomer resin (TPE-A) is expressed by its inherent viscosity (I.V). Its inherent viscosity has a value of 1.6 ~ 1.8 dl/g when measured in the solvent of 50/50 of phenol/tetrachloroethane (TCE).

TPE-A according to the present invention has a good elastic recovery rate and processability, compared with TPE without bisphenol-alt-ethylene glycol oligomer. That is, TPE-A can be processed at a low temperature since the melting temperature of resin is lowered by 10 ~ 20 °C compared with TPE without bisphenol-alt-ethylene glycol oligomer. It is desirable that the Melt Index (MI) of TPE-A has a range of 13 ~ 17g/10min under 230 °C and 2.16 kg, preferably 14 ~ 16g/10min.

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Furthermore, because bisphenol-alt-ethylene glycol oligomer lowers the melting temperature of TPE-A, TPE-A has good processability since its processing temperature at polymer processing after extrusion is low compared with TPE polymerized by only aromatic dicarboxylic acid, diol having a low molecular weight, and polyalkylene oxide. However, TPE-A itself has still such low melt viscosity or melt tension that it does not have optimal physical property

in the range of 35 ~ 70 mN, preferably 40 ~ 60 mN. The Melt Extension less than 35mN results in the decrease of thickness distribution and shape stability at the time of extrusion blowing, and more than 70mN results in the decrease of productability.

5 5. Melt Viscosity

Melt Viscosity is measured at the respective temperature of 230 °C, 240 °C and 250 °C within the range of extrusion shear rate by using RDS (Rheometric Dynamic Spectrometer).

10 6. Heat Distortion Temperature (HDT)

HDT of 1/4"specimen is determined under 4.16 kgf/cm² according to ASTM D 648.

7. Elastic Recovery Rate

15 A machine specimen injected by ASTM D 638 is installed to the jig by temperature, and the Elastic Recovery Rate of the specimen is measured after thermal treating for a desired time. Elastic Recovery Rate is determined as a ratio of the angle of specimen after annealing to the angle of specimen before annealing.

20 8. Impact Strength

Impact Strength is measured according to ASTM D 256 at both room temperature (23 °C) and low temperature (-40 °C).

9. Mechanical Physical Property

25 Tensile property and flexion property are determined according to ASTM D 638,790.

Example 1

30 34.6 weight% of DMT, 21.2 weight% of 1,4-butane diol, 40.2 weight% of PTMEG having the molecular weight of 2,000, 3.8 weight% of bisphenol-alt-ethylene glycol oligomer (n=1, HanNong

The composition and physical properties of the obtained TPE-B are listed at Tables 1 and 2 below.

Example 3

5 TPE-A is prepared according to the same procedure as Example 1 except that in the oligomerization, 36.3 weight% of DMT, 23.4 weight% of 1,4-butane diol, 39.7 weight% of PTMEG having the molecular weight of 2,000, 0.4 weight% of bisphenol-alt-ethylene glycol oligomer (n=1, HanNong WhaSung Koremul-BSA-20), and 0.065 weight% of glycerol are added to the oligomerization reactor, and 0.025 weight% of
10 TBT, a catalyst, is further added. Thereafter, in the polycondensation, 0.04 weight% of TBT, a catalyst, and 0.07 weight% of Irganox 1010, thermal stabilizer, are introduced to carry out the polycondensation. By using TPE-A thus obtained, TPE-B is prepared as the same composition as Example 1. The composition and physical properties of TPE-B thus obtained are listed in Tables 1 and 2 below.

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Example 4

TPE-A is prepared according to the same procedure as Example 1 except that in the oligomerization, 33.1 weight% of DMT, 19.3 weight% of 1,4-butane diol, 40.6 weight% of PTMEG having the molecular weight of 2,000, 6.8 weight% of
20 bisphenol-alt-ethylene glycol oligomer (n=1, HanNong WhaSung Koremul-BSA-20) and 0.059 weight% of glycerol are introduced to the oligomerization reactor, and 0.028 weight% of TBT, a catalyst, is further added. Thereafter, in the polycondensation, 0.043 weight% of TBT, a catalyst, and 0.07 weight% of Irganox 1010, thermal stabilizer, are added to carry out the polycondensation. By using TPE-A thus obtained, TPE-B is
25 prepared as the same composition as Example 1. The composition and physical properties of thus obtained TPE-B are listed in Tables 1 and 2 below.

Comparative Example 1

The same procedure as Example 1 is applied except that 96 weight% of TPE-A
30 prepared according to the same procedure as Example 1 is used and PBT is not used. The

obtained without bisphenol-alt-ethylene glycol oligomer is used and PBT is not used. The composition and physical properties of thus obtained TPE-B are listed in Tables 1 and 2 below.

5 Table 1

	TPE-B						
	TPE-A	TPE*	PBT	diisocyanate	carbodiimide	additional additive**	retention time
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(sec.)
Ex. 1	93		3	1.0	0.2	2.8	50~60
Ex. 2	76		20	1.0	0.2	2.8	50~60
Ex. 3	93		3	1.0	0.2	2.8	50~60
Ex. 4	93		3	1.0	0.2	2.8	50~60
Comp. Ex. 1	96		0	1.0	0.2	2.8	50~60
Comp. Ex. 2	66		30	1.0	0.2	2.8	50~60
Comp. Ex. 3	93		3	0	0	4.0	50~60
Comp. Ex. 4	93		3	0	0.2	3.8	50~60
Comp. Ex. 5	93		3	1.0	0.2	2.8	40
Comp. Ex. 6		96	0	1.0	0.2	2.8	50~60

* TPE: TPE polymerized without bisphenol-alt-ethylene glycol oligomer

** Additional additives: thermal stabilizer, antioxidant, lubricant, silicone-type master batch, and carbon black master batch

10 PBT: n=80~90, TRIBIT 1500 manufactured by Sam Yang Corp.

Diisocyanate: Lupranate MM103C manufactured by BASF

Carbodiimide: Stabaxol 1 manufactured by Bayer

Thermal stabilizer: 412S manufactured by SHIPRO Kasei Corp.

Antioxidant: Songnox 1076 manufactured by SongWon Industrial Corp.

15 Lubricant: EP861 manufactured by HENKEL Corp.

Silicone-type master batch: MB-50-010 manufactured by DOW CORNING Corp.

Carbon black master batch: BKA2 manufactured by Hyun Jin Chemical Co.

Table 2

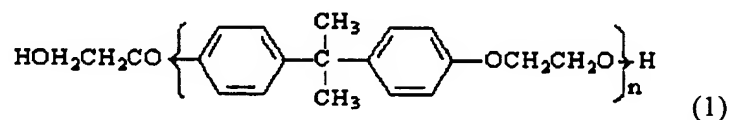
INDUSTRIAL AVAILABILITY

The polyester-type thermoplastic elastomer resin prepared by reactive extrusion by using hydroxyl carboxylic acid compound, diisocyanate, carbodiimide, and additional additives, after melt polymerization using bisphenol-alt-ethylene glycol oligomer according to the present invention, shows improved melt viscosity and melt index that results in good extrusion property, thermal resistance, chemical resistance, and durability, suitable for various automobile parts, particularly constant velocity joint boots and various bellows.

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CLAIMS

1. Thermoplastic elastomer resin (TPE-A) which comprises 30 ~ 45 weight% of aromatic dicarboxylic acid, 15 ~ 30 weight% of diol having a low molecular weight, 20 ~ 50 weight% of polyalkylene oxide, and 0.3 ~ 9.0 weight% of bisphenol-alt-ethylene glycol oligomer, represented by the following formula (1):



wherein n denotes a positive integer of 1 to 5.

2. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the inherent viscosity(I.V.) of TPE-A is 1.6 ~ 1.8 dl/g.
3. The thermoplastic elastomer resin (TPE-A) of claim 1, further comprising 0.05 ~ 10 weight% of glycerol.
4. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the aromatic dicarboxylic acid is selected from a group consisting of terephthalic acid, isophthalic acid, 1,5-dinaphthalenedicarboxylic acid, 2,6-dinaphthalenedicarboxylic acid, dimethyl terephthalate, dimethyl isophthalate, and mixtures thereof.
5. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the diol having a low molecular weight is selected from a group consisting of ethylene glycol, propylene glycol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,4-cyclohexane dimethanol, and mixtures thereof.
6. The thermoplastic elastomer resin (TPE-A) of claim 1 wherein the polyalkylene oxide is selected from a group consisting of polyoxyethylene glycol,

1.0 ~ 1.5.

12. The thermoplastic elastomer resin (TPE-B) wherein the inherent viscosity of PBT is 0.7 ~ 1.3 dl/g.

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13. A process for preparing thermoplastic elastomer resin (TPE-B) which comprises:
(a) melt polymerization of 30 ~ 45 weight% of aromatic dicarboxylic acid, 15 ~ 30 weight% of diol having a low molecular weight, 20 ~ 50 weight% of polyalkylene oxide, 0.3 ~ 9.0 weight% of diethyleneglycol bisphenol-A defined in claim 1, and 0.05 ~ 0.10 weight% of glycerol, to prepare TPE-A; and (b)
10 reactive extrusion of 66 ~ 96.85 weight% of TPE-A prepared in the above (a), 0.1 ~ 5.0 weight% of diisocyanate, and 0.05 ~ 1.0 weight% of carbodiimide, to prepare TPE-B.

- 15 14. The process of claim 13 wherein the diisocyanate is the modified product of 4,4-diphenylmethane diisocyanate defined in claim 10.

- 15 15. The process of claim 13 wherein the retention time in extruder in step (b) is between 50 and 80 seconds.

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